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Temperature-Programmed Desorption: Principles, Instrument Design, and Demonstration with $NaAlH_4$

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Abstract

This article is a brief introduction to temperature-programmed desorption (TPD), an analytical technique devised to analyze, in this case, materials for their potential as hydrogen storage materials. The principles and requirements of TPD are explained and the different components of a generic TPD apparatus are described. The construction of a modified TPD instrument from commercially available components is reported together with the control and acquisition technique used to create a TPD spectrum. The chemical and instrumental parameters to be considered in a typical TPD experiment and the analytical utility of the technique are demonstrated by the dehydrogenation of titanium-doped $NaAlH_4$ by means of thermally programmed desorption.

Keywords: temperature-programmed desorption; hydrogen storage materials; dehydrogenation

1. Introduction

Motivated by increasing oil prices, severe pollution problems, and political tension, many scientists are beginning to focus on hydrogen as a clean energy carrier and a renewable fuel for automobiles. One of the main obstacles to implementing a hydrogen economy is hydrogen storage on board a vehicle. Several types of hydrogen storage materials are being studied such as compressed hydrogen gas, cryogenic liquid hydrogen, chemical hydrides, complex metal hydrides, glass microspheres and carbon [1]. Among the most promising materials are complex metal hydrides due to their high hydrogen capacity and release of hydrogen at lower temperatures[2-5]. The practicality of using these materials for hydrogen storage depends on kinetics, hydrogen capacity, cost, and desorption parameters[6]. A useful analytical technique in the investigation of these compounds is temperature-programmed desorption (TPD). In a typical TPD experiment, a sample is heated (with temperature increasing linearly with time) and the partial pressures of the gases evolving from the sample are measured[7,8].

A range of TPD instruments exist for a variety of different applications. Thermo-volumetric analysis (TVA) is performed by a type of TPD instrument that maintains a constant system pressure as gas is evolved from the sample and determines the capacity of the material based on the travel of a piston[9]. Thermo-gravimetric analysis (TGA) uses a microbalance to determine weight changes of a sample corresponding to the gas evolved**.** While TGA measurements are commonly conducted to determine hydrogen storage capacity, the H_2 mass % is determined inductively by measuring the mass loss rather than the gas pressure change itself. Some TPD instruments also include a mass spectrometer to verify that the observed pressure change is associated with H_2 evolution only.

The TPD instrument constructed in this work will be labeled a Sievert's type apparatus. The instrument utilizes a pressure-volume-temperature method called PVT. The components consist of a known, calibrated volume and a high accuracy pressure transducer that together with precise temperature readings can generate accurate gas desorption measurements as a function of temperature. A pressure plot can be integrated to give kinetic data, phase transformation information, and a more accurate desorption temperature. This instrument has been modified from a traditional Sievert's instrument. This modified Sievert's instrument has been constructed with components rated to pressures in excess of 700 bar (10,000psi). With an operating pressure administratively limited to 570 bar (8,000psi), reversibility and kinetics of hydrogen storage materials can be investigated at high H_2 pressures. The other experimental adaptation from a traditional Sievert's PVT instrument is construction with Cajon VCR fittings for superior leak characteristics under vacuum conditions. Sorption experiments on nanoporous sorbent materials can be run under liquid nitrogen conditions at 77K[10].

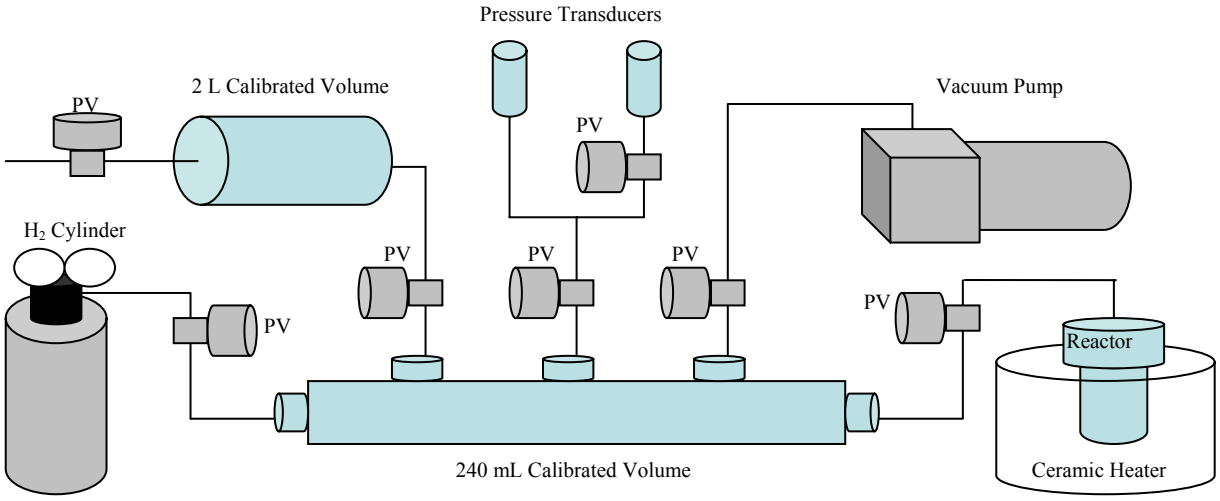

Fig. 1. Schematic of Sievert's gas sorption instrument. PV identifies pneumatic valves.

2. Experimental

2.1 Preparation of titanium-doped materials.

All sample preparations were performed under argon in a glove box. Sodium Aluminum Hydride ($NaAlH_4$) was purchased from Aldrich Chemical. $NaAlH_4$ was recrystallized from THF/pentane using standard Schlenk techniques[11] with oxygen and water-free solvents. $TiCl_3$ was used as purchased from Aldrich Chemical.

In a glove box, $NaAlH_4$ (0.89 g, 17 mmol) was combined with $TiCl_3$ (0.11 g, 0.6 mmol). Homogenized samples were prepared by ball milling for 60 minutes with a SPEX 8000 high energy mill at room temperature.

2.3 Instrument design

The Sievert's PVT system used in this desorption study contains a high pressure reactor vessel with a temperature controller unit (Parr Instrument Co.), a high vacuum pump (Alcatel Drytel 31), a low pressure transducer (BOC Edwards Barocel 600), a mid-range pressure transducer (MKS Baratron), and a high pressure transducer (GE Druck PMP4000). High pressure valves and pneumatic actuators (Autoclave) are paired with a solenoid valve stack (Festo). A Labview based software system was developed in house at Savannah River National Laboratory (SRNL) to control all hardware and record all system temperatures and pressures through a high precision National Instruments data acquisition system operated by a standard desktop computer. ASME certified 316L Stainless steel tubing 1/8"o.d. 0.035 wall-thickness is used for all flow lines. The experimental configuration is illustrated in Figure 1.

2.4 Desorption measurements

In order to investigate the thermal hydrogen release properties of novel materials, thermal desorption experiments are conducted. Typical experimental conditions are set with a pressure of ≤1 bar H_2. Also, larger volumes are used in order to prevent pressure equilibrium from occurring. Reversible hydrogen storage materials have an equilibrium pressure and temperature at which the dehydrided material rehydrogenates. When a large sample size is used for TPD with a small volume, the resulting pressure increase due to desorption may be sufficient to retard or inhibit complete dehydrogenation. The pressure increase affects reaction kinetics due to Le Châtlier's Principle. As the moles of H_2 desorption product increase, the reaction kinetics are slowed. Introduction of a larger volume reduces the effective pressure change thereby removing any kinetic anomalies to the desorption measurements.

The sample (0.50g) was loaded into the high pressure reactor under argon atmosphere and heated from room temperature to 300°C at a rate of 2°C per minute.[5] The amount of hydrogen desorption of the $NaAlH_4$ sample was observed as a function of temperature. Isothermal experiments are also conducted in which the sample is heated to a particular temperature and monitored for a period of a few hours in order to observe kinetic behavior.

2.5 Adsorption Measurements

Due to the requirement of high pressure compressed gases for rehydriding experiments, the authors feel it pertinent to remind readers of the hazard associated with the improper handling of compressed gas cylinders.

The capacity of hydrogen in materials is observed by pressure changes corresponding to adsorption based on temperature or time. A sample is loaded into a high pressure reactor in a glove box under argon atmosphere and is heated from room temperature to 300°C under an overpressure of hydrogen in a pre-measured volume. The pressure change, as monitored by a high accuracy pressure transducer is directly proportional to the amount of gas adsorbed by the sample. Due to the requirement of high hydrogen pressure for this experiment, safety risk is minimized by the use of a small calibrated volume as a hydrogen well to limit the quantity of high pressure gas being used.

2.6 Physisorption measurements

The physisorption and following thermal programmed desorption of carbon nanotubes is studied under low pressure and low temperature. The sample is loaded into a high pressure reactor in a glove box under argon atmosphere. The manifold and reactor are evacuated and the sample temperature is lowered to 77K by the submersion of the reactor into a liquid nitrogen dewar. Hydrogen is physisorbed onto the sample by applying on the order of 10 bar hydrogen pressure to the sample for 5 to 10 minutes while under low temperature conditions. For desorption measurements the hydrogen pressure is removed, the manifold is evacuated, and the sample is allowed to warm to room temperature. The pressure rise is monitored as a function of sample temperature.

3. Results and discussion

Titanium-doped $NaAlH_4$ was prepared for this demonstration by homogenizing freshly recrystallized hydride with $TiCl_3$ under an atmosphere of argon. The dehydriding of $NaAlH_4$ is thermodynamically favorable at moderate temperatures and is known to occur in these two reactions[12].

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + 3/2H_2 \quad (2)$$

A plot of the desorbed hydrogen weight percentage as a function of temperature is seen in Fig. 2. The discontinuity in the desorption curves reflects the difference in activation energies of the dehydriding reactions seen in Equations (1) and (2).

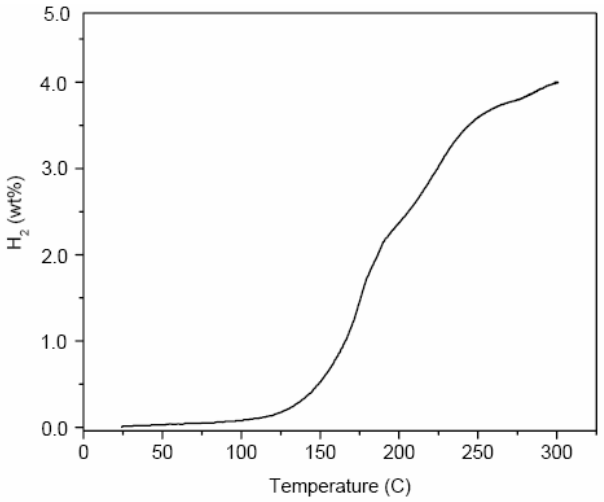

Figure 2. Thermal-programmed desorption (2°C min^{-1}) of hydrogen from Ti-doped sample of $NaAlH_4$.

A differential analysis of the desorption data yields Fig. 3. This differential plot gives information such as reaction rate and kinetics as well as a more defined desorption temperature for activation energy determination. Normalization of the differential curve to unity can also yield the percentage of total desorption occurring in each step. Symmetry of the differential desorption peaks may also be used to make statements about deformation within the crystalline environment during dehydrogenation.

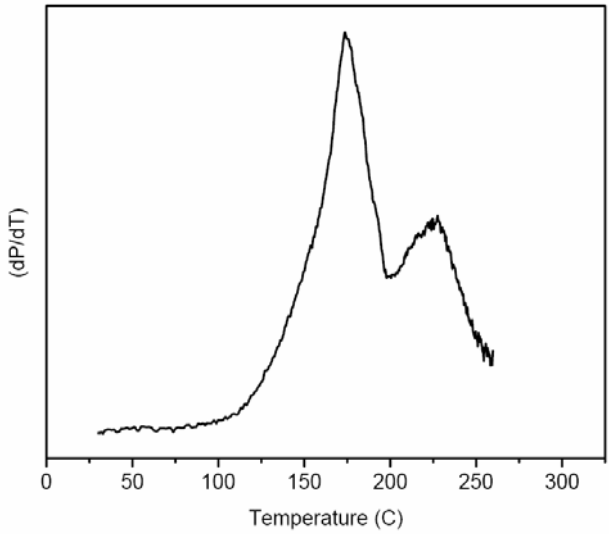

Figure 3. Differential plot of TPD data for $NaAlH_4$ relating dP/dT to temperature.

4. Conclusions

We have investigated the techniques of thermal-programmed desorption and the construction of a modified Sievert's instrument based on those techniques

has been completed. While this modified Sievert's type desorption device may not be the ideal instrument for the measurements needed to construct phase diagrams, or characterize the molecules evolved during heating, it is superior to most in scope of experiments and range of experimental parameters. Determination of the gravimetric density of hydrogen that is reversible at moderate temperatures is essential in the evaluation of metal hydrides and their viability as storage materials. Temperature-programmed desorption is an invaluable tool for the study of these materials. Commercial instruments are available, however this instrument possesses adaptations allowing it to operate under a wider range of conditions, widening its scope of experimental utility.

Acknowledgements

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